

Claims

1. A process for tetramerisation of olefins wherein the product stream of the process contains more than 30% of the tetramer olefin.
2. A process as claimed in Claim 1 which process includes the step of contacting an olefinic feedstream with a catalyst system containing a transition metal compound and a heteroatomic ligand.
3. A process as claimed in Claim 1 or Claim 2, wherein the feedstream includes an α -olefin and the product stream includes at least 30% of a tetramerised α -olefin monomer.
4. A process as claimed in any one of claims 1 to 3, wherein the olefinic feedstream includes ethylene and the product stream includes at least 30% 1-octene.
5. A process as claimed in any one of claims 1 to 3, wherein the olefinic feedstream includes ethylene and the product stream includes at least 40% 1-octene.
6. A process as claimed in any one of claims 1 to 3, wherein the olefinic feedstream includes ethylene and the product stream includes at least 50% 1-octene.
7. A process as claimed in any one of claims 1 to 3, wherein the olefinic feedstream includes ethylene and the product stream includes at least 60% 1-octene.
8. A process as claimed in any one of claims 1 to 3, wherein the olefinic feedstream includes ethylene and the product stream includes at least 70% 1-octene.
9. A process as claimed in any one of claims 1 to 8, wherein the olefinic feedstream includes ethylene and wherein the $(C_6 + C_8) : (C_4 + C_{10})$ ratio in the product stream is more than 2.5:1.

10. A process as claimed in any one of claims 1 to 9, wherein the olefinic feedstream includes ethylene and wherein the $C_8 : C_6$ ratio in the product stream is more than 1.
11. A process as claimed in any one of claims 4 to 10, wherein ethylene is contacted with the catalyst system at a pressure of more than 10 barg.
12. A process as claimed in any one of claims 1 to 11, wherein the heteroatomic ligand is described by the following general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C, and the R's are the same or different and each R is independently selected from any homo or hetero hydrocarbyl group and n and m for each R is independently determined by the respective valence and oxidation state of A and C.
13. A process as claimed in Claim 12, wherein A and/or C are potential electron donors for coordination with the transition metal.
14. A process as claimed in Claim 12 or Claim 13, wherein the heteroatomic ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth and nitrogen and B is a linking group between A and C, and R^1 , R^2 , R^3 and R^4 are independently selected from hydrocarbyl or hetero hydrocarbyl or substituted hydrocarbyl or substituted hetero hydrocarbyl groups.
15. A process as claimed in Claim 14, wherein the heteroatomic ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth and nitrogen and B is a linking group between A and C, and R^1 , R^2 , R^3 and R^4 are independently non-aromatic or aromatic, including hetero aromatic, groups.
16. A process as claimed in Claim 12, wherein the ligand contains multiples of $(R)_nA-B-C(R)_m$.

17. A process as claimed in Claim 15, wherein any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron donating.
18. A process as claimed in any one of claims 15 to 17, wherein R^1 , R^2 , R^3 and R^4 are independently aromatic, including hetero aromatic, groups and not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C.
19. A process as claimed in Claim 17 or Claim 18, wherein any non electron donating substituent is non polar.
20. A process as claimed in any one of claims 12 to 19, wherein B is selected from any one of a group comprising: organic linking groups comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; inorganic linking groups comprising single atom links; ionic links; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom or a halogen.
21. A process as claimed in any one of claims 12 to 20, wherein B is selected to be a single atom spacer.
22. A process as claimed in any one of claims 12 to 21, wherein B is selected to be $-N(R^5)-$, wherein R^5 is hydrogen or selected from the groups consisting of alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.
23. A process as claimed in any one of claims 12 to 22, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
24. A process as claimed in any one of claims 12 to 23, wherein A and C are independently phosphorus or phosphorus oxidised by S or Se or N or O.

25. A process as claimed in any one of claims 14 to 22 and 24, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising a benzyl, phenyl, tolyl, xylol, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranly group.
26. A process as claimed in Claim 25, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising a phenyl, tolyl, biphenyl, naphthyl, thiophenyl and ethyl group.
27. A process as claimed in any one of claims 1 to 22, 24 to 26 wherein the ligand is selected from any one of a group comprising
- (phenyl)₂PN(methyl)P(phenyl)₂, (phenyl)₂PN(pentyl)P(phenyl)₂,
 (phenyl)₂PN(phenyl)P(phenyl)₂, (phenyl)₂PN(*p*-methoxyphenyl)P(phenyl)₂,
 (phenyl)₂PN(*p*-⁴butylphenyl)P(phenyl)₂, (phenyl)₂PN((CH₂)₃-N-morpholine)P(phenyl)₂,
 (((phenyl)₂P)₂NCH₂CH₂)N, (phenyl)₂PN(Si(CH₃)₃)P(phenyl)₂,
 (ethyl)₂PN(methyl)P(ethyl)₂,
 (ethyl)₂PN(isopropyl)P(phenyl)₂, (ethyl)(phenyl)PN(methyl)P(ethyl)(phenyl),
 (ethyl)(phenyl)PN(isopropyl)P(phenyl)₂,
 (phenyl)₂P(=Se)N(isopropyl)P(phenyl)₂, (phenyl)₂PCH₂CH₂P(phenyl)₂, (*o*-ethylphenyl)(phenyl)PN(isopropyl)P(phenyl)₂, (*o*-methylphenyl)₂PN(isopropyl)P(*o*-methylphenyl)(phenyl),
 (phenyl)₂PN(benzyl)P(phenyl)₂, (phenyl)₂PN(1-cyclohexyl-ethyl)P(phenyl)₂,
 (phenyl)₂PN[CH₂CH₂CH₂Si(OMe)₃]P(phenyl)₂,
 (phenyl)₂PN(cyclohexyl)P(phenyl)₂, phenyl)₂PN(2-methylcyclohexyl)P(phenyl)₂, (phenyl)₂PN(allyl)P(phenyl)₂, (2-naphthyl)₂PN(methyl)P(2-naphthyl)₂, (*p*-biphenyl)₂PN(methyl)P(*p*-biphenyl)₂, (*p*-methylphenyl)₂PN(methyl)P(*p*-methylphenyl)₂, (2-thiophenyl)₂PN(methyl)P(2-thiophenyl)₂, (phenyl)₂PN(methyl)N(methyl)P(phenyl)₂, (*m*-methylphenyl)₂PN(methyl)P(*m*-methylphenyl)₂, (phenyl)₂PN(isopropyl)P(phenyl)₂, and (phenyl)₂P(=S)N(isopropyl)P(phenyl)₂.

28. A process as claimed in any one of the claims 1 to 27, which process includes the step of combining in any order a heteroatomic ligand with a transition metal precursor and an activator.
29. A process as claimed in any one of claims 1 to 28, which process includes the step of adding a pre-formed coordination complex, prepared using the heteroatomic ligand and a transition metal precursor, to a reaction mixture containing an activator.
30. A process as claimed in Claim 28, which includes the step of generating a heteroatomic coordination complex *in situ* from a transition metal precursor and a heteroatomic ligand.
31. A process as claimed in any one of the claims 2 to 30, wherein the transition metal is selected from any one of a group comprising chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
32. A process as claimed in any one of the claims 2 to 30, wherein the transition metal is chromium.
33. A process as claimed in any one of claims 28 to 30, wherein the transition metal precursor is selected from a group comprising of an inorganic salt, organic salt, a co-ordination complex and organometallic complex.
34. A process as claimed in Claim 33, wherein the transition metal precursor is selected from any one of a group comprising chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.
35. A process as claimed in any one of claims 28 to 34, wherein the transition metal is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.
36. A process as claimed in any one of claims 28 to 35, wherein the transition metal from a transition metal precursor and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.01:100 to 10 000:1.

37. A process as claimed in Claim 36, wherein the transition metal precursor and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.1:1 to 10:1.
38. A process as claimed in any one of claims 28 to 37, wherein the catalyst system includes an activator selected from any one of a group consisting of organoaluminium compounds, organoboron compounds, organic salts, such as methyllithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.
39. A process as claimed in any one of claims 28 to 38, wherein the activator is selected from alkylaluminoxanes.
40. A process as claimed in Claim 39, wherein the alkylaluminoxane, or mixtures thereof, is selected from a group which consists of methylaluminoxane (MAO), ethylaluminoxane (EAO) and modified alkylaluminoxanes (MMAO).
41. A process as claimed in Claim 39 or Claim 40, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 10 000:1.
42. A process as claimed in Claim 41, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 1000:1.
43. A process as claimed in Claim 42, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 300:1.
44. A process as claimed in any one of claims 39 to 43, which includes the step of adding to the catalyst system a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of alkylaluminoxane.

45. A process as claimed in any one of claims 2 to 44, which includes the step of mixing the components of the catalyst system at any temperature between -20°C and 250°C in the presence of an olefin.
46. A process as claimed in Claim 45, wherein the temperature range is between 20°C and 100°C
47. A process as claimed in claims 1 to 46, wherein methylcyclopentane and methylene cyclopentane are formed as products and independently make up at least 1% of the product stream of the process.
48. A tetramerisation catalyst system, which includes a transition metal and a heteroatomic ligand.
49. A catalyst system as claimed in Claim 48, wherein the heteroatomic ligand is described by the following general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C, and the R's are the same or different and each R is independently selected from any homo or hetero hydrocarbyl group and n and m for each R is independently determined by the respective valence and oxidation state of A and C.
50. A catalyst system as claimed in Claim 49, wherein A and/or C are a potential electron donor for coordination with the transition metal.
51. A catalyst system as claimed in Claim 49 or Claim 50, wherein the heteroatomic ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth and nitrogen and B is a linking group between A and C, and R^1 , R^2 , R^3 and R^4 are independently selected from hydrocarbyl or hetero hydrocarbyl or substituted hydrocarbyl or substituted hetero hydrocarbyl groups.
52. A catalyst system as claimed in Claim 51, wherein the heteroatomic ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises

phosphorus, arsenic, antimony, bismuth and nitrogen and B is a linking group between A and C, and R^1 , R^2 , R^3 and R^4 are independently non-aromatic or aromatic, including hetero aromatic, groups.

53. A catalyst system as claimed in Claim 49, wherein the ligand contains multiples of $(R)_nA-B-C(R)_m$.
54. A catalyst system as claimed in Claim 52 or Claim 53, wherein any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron donating.
55. A catalyst system as claimed in any one of claims 51 to 54, wherein R^1 , R^2 , R^3 and R^4 are independently aromatic, including hetero aromatic, groups and not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent the to atom bound to A or C.
56. A catalyst system as claimed in Claim 54 or Claim 55, wherein any non electron donating substituent is non polar.
57. A catalyst system as claimed in any one of claims 49 to 56, wherein B is selected from any one of a group comprising: organic linking groups comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; inorganic linking groups comprising single atom links; ionic links; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.
58. A catalyst system as claimed in any one of claims 49 to 57, wherein B is selected to be a single atom spacer.
59. A catalyst system as claimed in Claim 58, wherein B is selected to be $-N(R^5)-$, wherein R^5 is hydrogen or selected from the groups consisting of alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxy, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.

60. A catalyst system as claimed in any one of claims 49 to 59, wherein A and/or C is independently oxidised by S, Se, N or O where the valence of A and/or C allows for such oxidation.
61. A catalyst system as claimed in any one of claims 49 to 60, wherein A and C are independently phosphorus or phosphorus oxidised by S or Se or N or O.
62. A catalyst system as claimed in any one of claims 51 to 61, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising a benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranly group.
63. A catalyst system as claimed in any one of claims 51 to 62, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising a phenyl, tolyl, biphenyl, naphthyl, thiophenyl and ethyl group.
64. A catalyst system as claimed in any one of claims 49 to 59, 61 to 63, wherein the ligand is selected from any one of a group comprising
 (phenyl)₂PN(methyl)P(phenyl)₂, (phenyl)₂PN(pentyl)P(phenyl)₂,
 (phenyl)₂PN(phenyl)P(phenyl)₂, (phenyl)₂PN(*p*-methoxyphenyl)P(phenyl)₂,
 (phenyl)₂PN(*p*-⁴butylphenyl)P(phenyl)₂, (phenyl)₂PN((CH₂)₃-N-morpholine)P(phenyl)₂,
 (phenyl)₂PN(Si(CH₃)₃)P(phenyl)₂,
 (((phenyl)₂P)₂NCH₂CH₂)N, (ethyl)₂PN(methyl)P(ethyl)₂,
 (ethyl)₂PN(isopropyl)P(phenyl)₂, (ethyl)(phenyl)PN(methyl)P(ethyl)(phenyl),
 (ethyl)(phenyl)PN(isopropyl)P(phenyl)₂,
 (phenyl)₂P(=Se)N(isopropyl)P(phenyl)₂, (phenyl)₂PCH₂CH₂P(phenyl)₂, (*o*-ethylphenyl)(phenyl)PN(isopropyl)P(phenyl)₂, (*o*-methylphenyl)₂PN(isopropyl)P(*o*-methylphenyl)(phenyl),
 (phenyl)₂PN(benzyl)P(phenyl)₂, (phenyl)₂PN(1-cyclohexyl-ethyl)P(phenyl)₂,
 (phenyl)₂PN[CH₂CH₂CH₂Si(OMe₃)]P(phenyl)₂,
 (phenyl)₂PN(cyclohexyl)P(phenyl)₂, phenyl)₂PN(2-methylcyclohexyl)P(phenyl)₂,
 (phenyl)₂PN(allyl)P(phenyl)₂, (2-naphthyl)₂PN(methyl)P(2-naphthyl)₂,
 (*p*-biphenyl)₂PN(methyl)P(*p*-biphenyl)₂.

$(p\text{-methylphenyl})_2\text{PN}(\text{methyl})\text{P}(p\text{-methylphenyl})_2$,
 $(2\text{-thiophenyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-thiophenyl})_2$,
 $(\text{phenyl})_2\text{PN}(\text{methyl})\text{N}(\text{methyl})\text{P}(\text{phenyl})_2$, $(m\text{-methylphenyl})_2\text{PN}(\text{methyl})\text{P}(m\text{-methylphenyl})_2$,
 $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$, and
 $(\text{phenyl})_2\text{P}(=\text{S})\text{N}(\text{isopropyl})\text{P}(\text{phenyl})_2$.

65. A catalyst system as claimed in any one of the claims 49 to 64, wherein the transition metal is selected from any one of a group comprising chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
66. A catalyst system as claimed in any one of the claims 49 to 65, wherein the transition metal is chromium.
67. A catalyst system as claimed in Claim 66, wherein the transition metal is derived from a transition metal precursor selected from a group comprising of an inorganic salt, organic salt, a co-ordination complex and organometallic complex.
68. A catalyst system as claimed in Claim 67, wherein the transition metal precursor is selected from a group comprising chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl, and chromium (III) 2-ethylhexanoate.
69. A catalyst system as claimed in any one of claims 48 to 68, wherein the transition metal is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.
70. A catalyst system as claimed in claims 67 to 68 wherein the transition metal from a transition metal precursor and heteroatomic ligand have metal/ligand ratios from about 0.01:100 to 10 000:1.
71. A catalyst system as claimed in Claim 70, wherein the transition metal precursor and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.1:1 to 10:1.

72. A catalyst system as claimed in any one of the claims 48 to 71, which includes an activator.
73. A catalyst system as claimed in Claim 72, wherein the activator is selected from any one of a group consisting of organoaluminium compounds, organoboron compounds, organic salts, such as methyllithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.
74. A catalyst system as claimed in Claim 72, wherein the activator is selected from alkylaluminoxanes.
75. A process as claimed in Claim 74, wherein the alkylaluminoxane, or mixtures thereof, is selected from group which consists of methylaluminoxane (MAO), ethylaluminoxane (EAO) and modified alkylaluminoxanes (MMAO).
76. A catalyst system as claimed in Claim 74 or Claim 75, wherein the transition metal and the aluminoxane are in such proportions relative to each other to provide Al/metal ratios from about 1:1 to 10 000:1.
77. A catalyst system as claimed in Claim 76, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 1000:1.
78. A process as claimed in Claim 77, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 300:1.
79. A catalyst system as claimed in any one of claims 74 to 78, which includes a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of aluminoxane.
80. Use of a tetramerisation catalyst system as claimed in any one of claims 48 to 79 for the tetramerisation of olefins.
81. Use of a tetramerisation catalyst system as claimed in any one of claims 48 to 78 for the tetramerisation of ethylene.

82. Use of a ligand for a tetramerisation process as claimed in any one of claims 1 to 47.
83. Use of a ligand for a tetramerisation catalyst system as claimed in any one of claims 48 to 79.
84. An olefin tetramerisation process substantially as described herein.
85. An olefin tetramerisation catalyst system substantially as described herein.